Oxygen and sulfur adsorption on vicinal surfaces of copper and silver: Preferred adsorption sites

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We present an extensive density functional theory (DFT) study of adsorption site energetics for oxygen and sulfur adsorbed on two vicinal surfaces of Cu and Ag, with the goal of identifying the most stable adsorption site(s), identifying trends and common themes, and comparing with experimental work in the literature where possible. We also present benchmark calculations for adsorption on the flat (111) and (100) surfaces. The first vicinal surface is the (211), and results are similar for both metals. We find that the step-doubling reconstruction is favored with both adsorbates and is driven by the creation of a special stable fourfold hollow (4fh) site at the reconstructed step. Zig-zag chain structures consisting of \(X–M–X\) units (\(X = \text{chalcogen}, M = \text{metal}\)) at the step edge are considered, in which the special 4fh site is partially occupied. The zig-zag configuration is energetically competitive for oxygen but not sulfur. DFT results for oxygen agree with experiment in terms of the stability of the reconstruction, but contradict the original site assignment. The second vicinal surface is the (410), where again results are similar for both metals. For oxygen, DFT predicts that step sites are filled preferentially even at lowest coverage, followed by terrace sites, consistent with the experiment. For sulfur, in contrast, DFT predicts that terrace sites fill first. Oxygen forms \(O–M–O\) rows on the top edge of the step, where it occupies incomplete 4fh sites. This resolves an experimental ambiguity in the site assignment. For both the (211) and (410) surfaces, the interaction energy that stabilizes the \(X–M–X\) chain or row correlates with the linearity of the \(X–M–X\) unit, which may explain key differences between oxygen and sulfur. Published by AIP Publishing. https://doi.org/10.1063/1.5021091

I. INTRODUCTION

Surface steps play important roles in surface processes, including heterogeneous catalysis, thin film growth, nanowire formation, etching, and enantioselective separations. The low coordination and different steric environment of atoms at steps generally lead to different reactivity, relative to atoms on terraces. In some cases, this directly causes catalytic reactions to occur preferentially or exclusively at steps. For instance, Ru is the most active metal known for NO reduction. On the prototypical Ru(001) surface, steps are the active sites for NO dissociation, which is a key step in the reduction reaction.\textsuperscript{1} In other cases, the effect on catalytic reactions is less direct but equally profound. For example, a study of CO oxidation on surfaces vicinal to Pd(100) revealed that steps can disrupt a catalytically active oxide film and thereby inhibit the reaction.\textsuperscript{2} In the growth of thin films, steps are often heterogeneous nucleation sites and can engender smooth step-flow growth under appropriate conditions;\textsuperscript{3,4} the reverse can be true under etching conditions.\textsuperscript{5} In a similar vein, steps can serve as templates for formation of one-dimensional nanowires along the step.\textsuperscript{6} Regarding enantioselective separations, some steps present atomic configurations that are naturally chiral and can be used to separate chiral adsorbates; Cu, in particular, has been used for this purpose.\textsuperscript{7} Of course, on nanoparticles, the atomic configurations associated with steps are abundant, and in some cases the special properties of nanoparticles may be entirely due to the high density of low-coordination sites, e.g., in CO oxidation on Au.\textsuperscript{8} Fundamental aspects of adsorption and reaction, on or near steps, have been reviewed comprehensively by Vattuone \textit{et al.}\textsuperscript{9,10}

Understanding the adsorption site of atoms or molecules at steps is basic to understanding the role that steps play in any of the above processes. In this paper, we focus on one particular class of adsorbates (the most common chalcogens, oxygen and sulfur). Our goal is to identify the preferred adsorption sites on highly stepped surfaces of two coinage metals (Cu, Ag), using density functional theory (DFT). This choice of systems—chalcogens on coinage metals—is motivated by its relevance to heterogeneous catalysis, plasmonics, corrosion, surface functionalization, and other applications. Two stepped surfaces are examined—(211) and (410)—both of which can be regarded as vicinal to (100). [The (211) surface can alternatively be regarded as vicinal to (111).] Our emphasis is on comparing theoretical results with experimental data for single-crystal surfaces and identifying trends and common themes within this group. In some cases—particularly for the O/Cu systems—high-level experimental data are available, but little or no theoretical analysis has been

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applied, perhaps because DFT calculations on vicinal surfaces are somewhat unconventional and demanding or because the experimental studies preceded wide implementation of DFT.

Some previous DFT work does exist. Most comprehensive is a DFT study by Peterson et al., which examined oxygen on fcc(211) surfaces of late transition metals, hence overlapping with two of the systems considered in this paper—O/Cu(211) and O/Ag(211). However, that study’s purpose was to compare adsorption on stepped surfaces with adsorption on small clusters in order to identify finite size effects, rather than to correlate with experimental data for extended vicinal surfaces. The prior DFT work provides some touchpoints for the present effort.

Our confidence in the results from the present DFT calculations is based largely on past successes with adsorption of chalcogens on coinage metals, where detailed comparisons with high-quality experimental data served to indicate the successes or shortcomings of DFT. Most notably, DFT successfully provided an interpretation of scanning tunneling microscopy (STM) data for sulfur adsorption and sulfur-induced reconstruction at steps on Cu(111), for selenium-induced faceting of steps on Cu(111), and for adsorption of sulfur atoms at steps (without reconstruction or faceting) on Cu(100). Various aspects of the experimental data—adsorption sites, coverage dependence, and image features—were consistent with DFT results.

It is well known that steps of some vicinal Ag surfaces oxidize readily even at or below room temperature. However, it is also well known that oxidation is very sensitive to the Ag atomic structure; for example, Ag(410) is unreactive under conditions where the (210) oxidizes readily. For the Cu and Ag surfaces considered in this paper, there is no report of low-temperature oxidation; furthermore, we examine the low-coverage regime where oxidation is less likely. Therefore, we consider only chemisorbed structures.

This study is presented as follows: Section II contains the computational details. Section III is a presentation and discussion of oxygen adsorption on the low-index (111) and (100) surfaces of Cu and Ag. We then present results for oxygen on Cu(211) and Ag(211), followed by oxygen on Cu(410) and Ag(410). Section IV focuses on sulfur adsorption on the low-index surfaces, followed by the vicinal surfaces. This section is relatively brief because experimental data for sulfur at steps are scarce, but nonetheless, the comparison with oxygen is interesting and the DFT results may be useful for interpreting future experiments. Section V is an overall discussion, and Sec. VI concludes the paper.

II. METHODS

We performed density functional theory (DFT) calculations of O and S adsorption on the (211) and (410) surfaces of Cu and Ag using the plane-wave VASP code, with the projector augmented wave (PAW) potentials, optimized for the Perdew-Burke-Ernzerhof (PBE) functional. The plane wave energy cutoff was 400 eV for adsorption of O and 280 eV for adsorption of S. Slightly different theoretical lattice constants were used depending on the energy cutoff. For Cu, the bulk lattice constant was \( a_b = 0.3636 \) nm for 400 eV and \( a_b = 0.3641 \) nm for 280 eV. For Ag, \( a_b = 0.4147 \) nm for 400 eV and \( a_b = 0.4149 \) nm for 280 eV. Sometimes it was more convenient to use the nearest-neighbor distance in the fcc crystal, \( a_r = a_b/\sqrt{2} \).

To construct the supercells used in plane wave DFT calculations, 3 basis vectors \( b \) are useful since a stepped surface is three-dimensional. With respect to the surface Miller indices \((hkl)\), we chose one axis \( b_1 \) to be parallel to \([hkl]\) and chose the other two vectors (which are orthogonal to \( b_1 \)) to define the desired shape and area. For the (211) surface, a convenient choice of the primitive surface cell has \( b_1 \) parallel to \([0, 1/2, -1/2]\) and \( b_2 \) parallel to \([-1, 1, 1]\), forming an \((a_x \times \sqrt{6}a_y)\) rectangle. This will be denoted \((1 \times \sqrt{6})/90^\circ\), where the angle \(90^\circ\) in this case) is between basis vectors \( b_1 \) and \( b_2 \). For the (410) surface, the primitive surface cell has \( b_1 \) aligned with \([0, 0, 1]\) and \( b_2 \) aligned with \([-1/2, 2, 1/2]\), forming \((\sqrt{2} \times 3)/76^\circ\). For clarification, see Fig. S1 of the supplementary material. The supercells so chosen were always orthorhombic.

Calculations were performed using periodic slabs with various thicknesses in terms of number of layers \( L \), separated by 1.2 nm of vacuum. Results were averaged over a number of layers in order to reduce errors from quantum size effects (QSE) and finite \( k \)-point grids. A layer is defined as a plane of atoms perpendicular to \( b_3 \). Because these surfaces are vicinal, layers are less dense and more closely spaced than for low-index surfaces. Values of energy are usually trailed by one or two digits in the parentheses. This is the numerical uncertainty or error in meV, where the digits indicate the standard deviations divided by the number of slabs for all \( L \) in that calculation. The Appendix contains examples of the averaging procedure, estimates of numerical errors, and illustrations of QSE due to the slab thickness.

All atoms were allowed to relax except for the bottom two layers for the (211) surface and the bottom four layers for the (410) surface. A \( \Gamma \)-centered \([l24b_1l] \times [l24b_2l] \times 1\) \( k \)-point grid was used for a supercell with side lengths \( b_1 \) and \( b_2 \), where \([lxl] \) denotes the integer that is nearest to the real number \( x \). Bulk and surface calculations were performed with no spin polarization, while the reference energies of O\(_2\) and S\(_2\) were calculated with triplet spin states.

To assess the stability of various metal-adsorbate complexes, we defined the chemical potential of an adsorbate \( \chi = (O, S) \) as

\[
\mu_{\chi} = [E(M_mX_n + \text{slab}_{(hkl)}) - E(\text{slab}_{(hkl)}) - m \mu_M] / n - E(X_{2g}) / 2,
\]

where \( E \) is the energy, \( \mu_M \) is the cohesive energy of bulk metal \( M \), and \( m \) and \( n \) define the stoichiometry of the complex \( M_mX_n \). In this paper, we used the unconstructed (but relaxed) clean \((hkl)\) surface for the “slab” in Eq. (1). For adsorption on the unconstructed surface, \( m = 0 \) and \( \mu_{\chi} \) is simply the adsorption energy. For a reconstructed surface, however, we can view the outer layer of metal atoms as part of a metal-adsorbate complex. Thus using Eq. (1), the chemical potential \( \mu_{\chi} \) also takes into account the (free) energy cost of the reconstruction.
III. OXYGEN ADSORPTION ON COPPER AND SILVER SURFACES

A. Oxygen on the low-index (111) and (100) surfaces of Cu and Ag

On real surfaces, adsorption on steps always competes with adsorption on terraces, provided that the adsorbate can sample an area that encompasses both types of features. It is thus relevant to consider, briefly, the adsorption energies of O on the low-index (100) and (111) terraces. These are shown in Fig. 1. Details of the calculations, and values for the results, are given in the supplementary material. Following Abufager et al.,58 we plot \( \mu_X \) as a function of \( 1/\theta_X \). With this choice of axes, the stability of the system can be represented by the convex hull (solid line segments). In all cases, the hull falls as \( 1/\theta_X \) increases (\( \theta_X \) decreases) due to decreasing lateral interactions. One interesting feature is that, for a specific metal at fixed \( \theta_O \), oxygen is always much more stable on the (100) surface than that on the (111) surface, i.e., oxygen is more stable at a fourfold hollow (4fh) site than a threefold hollow (3fh) site. This is true for both Cu and Ag and can be rationalized straightforwardly in terms of localized bonding. Also, adsorption is much stronger on Cu than on Ag, for given \( \theta_S \) and \( (hkl) \), which is consistent with general expectation and also with trends in heats of formation among oxides of Cu and Ag.59

B. Oxygen on (211) vicinal surfaces

1. Oxygen on Cu(211)

Figure 2 shows configurations and energetics of O on various adsorption sites of unreconstructed Cu(211) surfaces. There are several ways to view the fcc(211) surface—as a stepped (111) surface (top panels), a faceted surface (middle panels), or a stepped (100) surface (bottom panels). The three left-most columns present three adsorption configurations that we call single-row structures because the adsorbate forms a single row parallel to the step. In each, O occupies only a single type of adsorption site on the unreconstructed (U) surface. U-A is a 4fh site, while U-B is a 3fh fcc site and U-C is a 3fh hcp site. The adsorption energies are also shown in Fig. 2, derived by averaging over slabs from \( L = 14–24 \). Among the three single-row structures, U-C (the 3fh site nearest the step, i.e., the hcp site) is favored. This shows a failure of the generalization noted in Sec. III A, i.e., that O adsorption is more favorable at 4fh than at 3fh sites. Adsorption at steps cannot be predicted based on data for terraces alone.

The conclusion that U-C is most stable is consistent with prior work by Peterson et al.13 using DFT with the RPBE23 functional and by Xu and Mavrikakis11 with the PW91 functional. Both examined single-row structures, and both found...
the U-C site to be most favorable. Not considered in either previous study, however, was the double row structure labeled U-A2 in Fig. 2. It has a zig-zag O–Cu–O structure and is more stable than any of the single-row structures.

However, all of these configurations have questionable relevance to experiment. Thompson and Fadley studied the O/Cu(211) system using X-ray photoelectron diffraction (XPD) and low-energy electron diffraction (LEED) and observed a double step reconstruction, in which contiguous (111) facets are expanded. This reconstruction was later confirmed by Witte et al. using a variety of experimental techniques. We therefore perform DFT calculations of O adsorption on the double-step reconstructed (R) surface. Such calculations have not been reported previously. Results are shown in the lower part of Fig. 2. Again, three different types of top views are presented. The five left-most columns are single-row structures, where R-A and R-C are 4fh sites, while R-B, R-D, R-E, and R-F are 3fh sites. The most stable adsorption site is the 4fh site at the top of the vertical wall of the (100) step, labeled R-C. Even more significantly, $\mu_O$ for the R-C configuration is lower (more stable) than all configurations of the unreconstructed surface (see Fig. 2). As mentioned in Sec. II, the chemical potential $\mu_O$ takes into account the energy cost of reconstruction. Thus DFT shows that there is a driving force for double-step reconstruction of O/Cu(211), confirming experiments.

By comparing XPD experimental data with scattering calculations, Thompson and Fadley concluded that the most likely adsorption site is R-A, but they did not rule out some occupation of R-C sites. DFT, on the other hand, shows that R-C is more stable than R-A. Because of this discrepancy, we performed additional DFT calculations using different exchange-functionals to test the robustness of the DFT result. Table I compares some selected configurations from Fig. 2,
TABLE I. Values of $\mu_O$ in eV, obtained using different exchange-correlation functionals in DFT, for configurations of O/Cu(211). PBE-optimized geometries are used for optB88-vdW and SCAN.

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>PBE</th>
<th>optB88-vdW</th>
<th>SCAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-A</td>
<td>-2.357(2)</td>
<td>-1.722(2)</td>
<td>-1.995(6)</td>
<td>-2.195(11)</td>
</tr>
<tr>
<td>U-C</td>
<td>-2.371(2)</td>
<td>-1.824(3)</td>
<td>-2.034(3)</td>
<td>-2.200(8)</td>
</tr>
<tr>
<td>U-A2</td>
<td>-2.435(2)</td>
<td>-1.861(2)</td>
<td>-2.107(5)</td>
<td>-2.205(9)</td>
</tr>
<tr>
<td>R-A</td>
<td>-2.260(8)</td>
<td>-1.642(8)</td>
<td>-1.888(7)</td>
<td>-2.116(3)</td>
</tr>
<tr>
<td>R-C</td>
<td>-2.651(7)</td>
<td>-1.992(7)</td>
<td>-2.185(6)</td>
<td>-2.428(2)</td>
</tr>
<tr>
<td>R-A2</td>
<td>-2.610(2)</td>
<td>-2.024(2)</td>
<td>-2.247(2)</td>
<td>-2.380(3)</td>
</tr>
</tbody>
</table>

using local-density approximation (LDA), optB88-vdW,26 and strongly-constrained and appropriately normed (SCAN) meta-generalized gradient approximation.27 All functionals predict that R-C is much more stable than R-A (by 0.3-0.4 eV). All functionals also confirm that R-C is more stable than any of the unreconstructed configurations (by 0.1-0.3 eV).

Aside from direct DFT energy calculations, there is another argument for the R-C site to be more favorable than R-A. We know that clean Cu(211) does not reconstruct.24,25 Therefore adsorption of O on the reconstructed Cu(211) must be stronger than on the unreconstructed surface. As Fig. 3 shows, configuration U-A has 4 Cu–O bonds that are 0.19 nm to 0.21 nm long (with Cu atoms 1-4) and 2 between 0.27 and 0.30 nm (with Cu atoms 5-6). R-A is very similar to U-A, and it fits the same description. Thus, an oxygen atom adsorbed at the 4f site at the bottom of a step is in the same local environment regardless of whether the surface is reconstructed or not. Adsorption in this site provides little energetic driver for reconstruction; indeed, $\mu_O$ differs by only 0.08 eV between U-A and R-A. On the other hand, the R-C adsorption site is only available after reconstruction. There, oxygen does not have the last Cu–O bond (to Cu atom 6). The interaction of oxygen with this Cu atom may be repulsive. If so, then in the R-C configuration, oxygen can avoid this row of Cu atoms and thus is more stable than R-A, confirmed by the 0.35 eV difference between $\mu_O$ for R-A and R-C.

Figure 2 also shows a double-row structure (R-A2) that has the same zig-zag O–Cu–O motif as U-A2, combining 4f and 3fh hcp sites (R-C and R-F, respectively). Its value of $\mu_O$ is lower than the average $\mu_O$ of the two constituent adsorption sites, indicating an attractive interaction between two oxygen atoms through the central Cu atom. The value of $\mu_O$ is slightly lower for R-A2 than for R-C (0.03 eV) using PBE. Inspection of Table I shows that this hierarchy is not robust. For one of the alternative functionals, optB88-vdW, R-A2 has slightly lower $\mu_O$, as is the case with PBE. But with the two other functionals—LDA and SCAN—R-A2 has slightly higher $\mu_O$. Based on both the small energy difference and the functional-dependence, we conclude that DFT results are not definitive regarding the relative stability of R-C vs. R-A2 and that there is a physical uncertainty in PBE of about 0.03 eV (meaning, if two values fall within 0.03 eV, they are not significantly different). Note that this value of the physical uncertainty applies only to the type of comparison being made in this paper, i.e., comparisons among adsorption sites on stepped surfaces, and that the physical uncertainty is different than the numerical uncertainty defined in Sec. II and the Appendix.

A natural question is whether the double step reconstruction observed in experiments corresponds to R-C (with ideal oxygen coverage $\theta_O = 0.10$) or R-A2 ($\theta_O = 0.2$), where $\theta_O$ is defined as the number of adsorbed O atoms per area of the (100) surface unit cell. Because they are nearly degenerate in energy, we speculate that a transition from R-C to R-A2 could occur with increasing oxygen coverage or that the structure could depend on other experimental parameters such as temperature.

Thompson and Fadley24 made their measurements at $\theta_O = 0.10$, which should be ideal for the R-C structure on the basis of coverage alone. However, in the experiments of Witte et al.,25 after low O$_2$ exposure followed by annealing, well-separated long double-step rows coexisted with unreconstructed surface regions [Fig. 7(b) in Ref. 25]. This observation suggests that an attractive interaction is involved in forming the reconstructed steps. Such an effect can be more readily explained by the direct attractive interaction in R-A2 noted above, rather than any small interaction between O atoms along the step edges as in R-C. Furthermore, the R-A2 structure induces strain, which may be responsible for the experimentally observed modulation of 3.8 nm along the step edge.25 Thus, it is likely that R-A2 is formed under the conditions of these particular experiments and may form under the conditions used by Thompson and Fadley as well. Notably, Thompson and Fadley24 did not consider the possibility of the R-A2 structure when fitting their XPD data, which may contribute to the apparent discrepancy between experiment and theory.

In summary, DFT shows there is a driving force for double-step reconstruction of O/Cu(211), confirming experiments.24,25 DFT also shows that R-A, the adsorption site

FIG. 3. Cu–O bond lengths, $l_b$, and depictions of Cu atoms 1-6, for the configurations (a) U-A, (b) R-A, and (c) R-C. Small red circles are oxygen atoms, and larger white/gray circles are Cu atoms, with darker shades indicating further distance from the viewer (deeper levels). The viewing direction is [211].
originally identified from XPD, is not the most stable adsorption site for oxygen on reconstructed Cu(211). Two other adsorption configurations, R-C and R-A2, have maximum stability, but the energy difference between them is small and their relative stability depends on the functional used in DFT. Possibly, both could be observed in experiment depending on experimental parameters such as coverage or temperature. There is some indication that R-A2 was observed in a prior experiment.25

2. Oxygen on Ag(211)

The optimized configurations for O/Ag(211) are almost indistinguishable from O/Cu(211), so the structures of Fig. 2 are applicable. However, there are some differences in the energetics. First, the value of adsorption energy at a given site is always more positive for Ag than for Cu, mimicking the trend for the low-index surfaces. Second, on the unreconstructed Ag surface, the U-A site (4fh) is more stable than the U-C site (3fh hcp). Petersen et al.13 obtained similar DFT results for this system, i.e., they found that O atoms are most stable on the U-A site (4fh) on Ag(211). However, they did not consider the U-A2 site, which is most stable of all among the unreconstructed models, as was also true for O/Cu(211).

Among the reconstructed surfaces, results for O/Ag(211) are analogous to those for O/Cu(211). The R-C configuration is more stable than any of the unreconstructed models. Thus we anticipate the reconstruction of Ag(211) upon oxygen exposure. Furthermore, R-A2 is slightly more stable than R-C among the reconstructed configurations, although the difference is only 0.03 eV. Following the analysis of O/Cu(211) in Sec. III A 1, this suggests that both R-A2 and R-C could be observable in experiment.

Somewhat surprisingly, it appears that no experimental results are available for O/Ag(211).

C. Oxygen on (410) vicinal surfaces

1. Oxygen on Cu(410)

Figure 4 shows various configurations and \(\mu_0\) values for O/Cu(410), where Cu(410) can be viewed as vicinal to (100) with open step edges. The models are grouped according to coverage, from low (L) \(\theta_0 = 0.12\), to medium (M) \(\theta_0 = 0.24\), to high (H) \(\theta_0 = 0.49\).

Among configurations L-A to L-D, the 4fh site L-A, at the bottom of a step, has the highest \(\mu_0\). The two 4fh sites L-B and L-C, and the partial 4fh site L-D, all have lower self-similar \(\mu_0\) values. Thus, there is no strong energetic distinction between adsorption at the top of the step edge (L-D) or on the (100) facet (L-B and L-C), but adsorption is unfavorable at the bottom of the step (L-A). The relative low stability of L-A may be due to the presence of two Cu atoms in the step that are close to the O atom, about 0.29 nm away, in positions analogous to that of Cu atom 6 in Fig. 3 for O/Cu(211).

In configurations M-A to M-D, the adsorption sites are the same as in the L-series, but the spacing between oxygen atoms in the direction parallel to the steps is smaller in the M-series than in the L-series—\(\sqrt{2}a_0\) vs. \(2\sqrt{2}a_0\), respectively. The fact that M-A, M-B, and M-C are less stable than their L-counterparts indicates a repulsive interaction between O atoms at a distance of \(\sqrt{2}a_0\) when they are adsorbed on the (100) terraces or at the bottom of the step edge. However, M-D is more stable than L-D, indicating an attractive interaction at \(\sqrt{2}a_0\) when O adsorbs at the top edge of a step.

Of all low- and medium-coverage configurations, the incomplete 4fh site M-D has lowest \(\mu_0 = -2.056\) eV. This value is significantly lower than any other L- or M-site, and lower than any \(\mu_0\) on the flat (100) surface (cf. Fig. 1). We thus predict that this site should fill first, even at lowest coverage.

Oxygen adsorption on Cu(410) has been studied extensively.24,28–37 The Cu(410) surface is particularly stable when exposed to oxygen and several surfaces vicinal to Cu(100) to (410) in the presence of adsorbed oxygen.38,39 The early study by Thompson and Fadley24 showed that the clean Cu(410) surface does not reconstruct. This is true also for the oxygen-covered surface with \(\theta_0 = 0.1\).24 Our DFT results resolve this ambiguity by showing that M-D is most stable.

At high coverage, ca. \(\theta_0 \geq 0.3\), terrace sites are also occupied, which is the conclusion of even earlier LEED studies of Perdereau and Rhead.28 These authors observed a \((2 \times 2)\) structure in low-energy electron diffraction and proposed structure H-A in Fig. 4,28 which was confirmed by Thompson and Fadley’s XPD work.24 However, the structural
assignment later fell under scrutiny\textsuperscript{29,36} in part because it is closely related to the missing-row (\(\sqrt{2} \times \sqrt{2}\))R45\(^\circ\) structure of O/Cu(100).\textsuperscript{40–43} This led to some debate about whether there is a similar missing row reconstruction on Cu(410), where the rows of Cu atoms near the bottom of the step edges would be missing. Thus there has been extensive consideration of the H-type configurations in Fig. 4. Configuration H-A shows the DFT optimized structure without any missing rows, H-B shows a structure with the row of Cu atoms near the bottom of the steps removed, and H-C shows a structure with the second row from the top of the steps removed instead. Positions of the missing rows are marked by horizontal arrows in Fig. 4. All these structures have been analyzed using different experimental techniques,\textsuperscript{29,37} with the more recent studies\textsuperscript{30,36} suggesting that there are no missing rows. Our DFT results confirm this recent conclusion as well as the early work,\textsuperscript{24,28} by showing that H-A is the most stable configuration for O/Cu(410) at high coverage. It is, however, significantly less stable than M-D, consistent with the experimental observation that these two structures develop sequentially with increasing coverage.\textsuperscript{24}

As far as we know, there has been no previous comparison of energetics for various O adsorption sites on Cu(410) using DFT, for any coverage. However, there has been a previous DFT calculation of the optimized high-coverage configuration (H-A) showing that it is structurally consistent with surface X-ray diffraction data.\textsuperscript{30}

### 2. Oxygen on Ag(410)

The trends for O/Ag(410) are very similar to those for O/Cu(410). With reference to Fig. 4, the M-D structure, where O forms zig-zag O–Ag–O chains at the steps, has lowest \(\mu_O\) and H-A is second but significantly higher. This leads to an expectation that M-D and H-A will populate sequentially. Also, the high-coverage missing-row structures H-B and H-C are less stable than H-A, so no missing-row structures are anticipated.

The main difference between O/Ag(410) and O/Cu(410) is that among the low-coverage (L) structures, O/Ag(410) is most stable at L-B rather than L-D. At L-B, the oxygen atom is in a 4fh site somewhat removed from the lower step edge. The reason for this difference between Ag and Cu is unclear.

The importance of steps for oxygen adsorption on Ag(410) has been observed by Savio, Vattuone, and Rocca\textsuperscript{44,45} through vibrational spectroscopy, though specific adsorption sites were not assigned. Bonini et al.\textsuperscript{12} studied O adsorption on the Ag(211) and Ag(410) surfaces using DFT. Their results (using PWscf and PHONO package) are consistent with results reported here. Specifically, for low coverage (\(\theta_O = 0.12\)), the most stable configuration is L-B (called T2 in Ref. 12). At \(\theta_O = 0.24\), the most stable site is M-D (called A-A in Ref. 12).

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**FIG. 5.** Adsorption energy of sulfur on (111) and (100) surfaces of Cu and Ag, as a function of 1/\(\theta_S\) (bottom abscissa) or \(\theta_S\) (top abscissa). Each point represents a different adsorption configuration. The configurations that are predicted to exist in thermodynamic equilibrium are those which fall on the solid line segments (on the convex hull). Error bars show numerical uncertainties in \(\mu_S\) as defined in Sec. II and the Appendix.
IV. SULFUR ADSORPTION ON COPPER AND SILVER SURFACES

A. Sulfur on the low-index (111) and (100) surfaces of Cu and Ag

Values of $\mu_S$ are shown vs. $1/\theta_S$ in Fig. 5, for sulfur adsorbed on the low-index (111) and (100) surfaces of Cu and Ag in various configurations. Details of the calculations, and exact values of the results, are given in the supplementary material. As for oxygen, sulfur adsorption is always much stronger on the (100) surface than on the (111) surface, for fixed metal and given $\theta_S$. This supports a long-held view that sulfur adsorbs more strongly at 4fh sites than 3fh sites on the late transition metals, which can drive surface reconstruction.\textsuperscript{46,47} Also, sulfur adsorption is much stronger on Cu than on Ag, for given $\theta_S$ and (hkl), which mimics the trend for oxygen.

Previously, we have published values of $\mu_S$ for some of the configurations represented in Fig. 5.\textsuperscript{14,18,20,48,49} However, the data in Fig. 5 are significantly improved by using thicker slabs and/or denser k-points than in most of the earlier work. Also, previously we have not compared trends across different systems as is done in Fig. 5; rather, the focus has been on determining relative stabilities of various phases within each system individually.

B. Sulfur on (211) vicinal surfaces

Figure 6 shows optimized configurations for S/Cu(211), together with values of $\mu_S$. Among the unreconstructed surfaces, single-row 4fh U-A is most stable and double-row U-A2 is significantly less stable. This contrasts O/Cu(211) and O/Ag(211), where U-A2 was most stable.

![Adsorption configurations for sulfur on Cu(211) and Ag(211)](attachment:adsorption_configurations.png)

**FIG. 6.** Adsorption configurations for sulfur (small yellow circles) on unreconstructed (U) and reconstructed (R) surfaces of Cu(211) and Ag(211). White/gray circles are Cu atoms, with darker shades indicating increasing distance from the viewer. For each configuration, three views are shown, corresponding to the schematics at left. For each configuration, values of $\mu_S$ are listed for Cu (top value) and Ag (bottom value), in eV.
FIG. 7. Adsorption configurations of sulfur (small yellow circles) on the vicinal (410) surfaces of Cu and Ag. White/gray circles are Cu atoms, with darker shades indicating increasing distance from the viewer. The viewing direction is [100]. Configurations are named according to coverage: low (L), medium (M), or high (H). For each configuration, values of $\mu_S$ are listed for Cu (top value) and Ag (bottom value), in eV.

On the double-step reconstructed surface, results are similar to O/Cu(211) and O/Ag(211). The R-C site is most stable, significantly more so than any configuration on the unreconstructed surface. Hence reconstruction is predicted to occur for S/Cu(211) also. However, the R-A2 configuration is not close to R-C, so only R-C should be observed in experiment.

DFT results for S/Ag(211) are also given in Fig. 6. Behavior is very similar to S/Cu(211), and double step reconstruction is predicted. Only R-C is expected to be observed.

As far as we know, there is no experimental report regarding S adsorption on Cu(211) or Ag(211).

C. Sulfur on (410) vicinal surfaces

DFT results for S/Cu(410) are shown in Fig. 7. Many features are different than O/Cu(410) and O/Ag(410). First, a 4fh site toward the middle of the (100) facet, L-C, is most stable, not only among the L-sites but also among all the sites. Hence L-C replaces M-D as the overall favored site. M-D is not even favored among the M subgroup. Second, as $\theta_S$ increases from L to M, $\mu_S$ for each adsorption site increases, indicating repulsive interactions between S at $\sqrt{2}a_s$ for all configurations. Thus, in contrast to oxygen, the S–Cu chain at the step edge in M-D provides no stabilization relative to L-D. Third, at high coverage, one of the missing-row configurations (H-B) is slightly more stable than either H-A or H-C, leading to the possibility of observing such a reconstruction in this system. However, we caution that no extensive search for optimal configurations at this coverage has been conducted.

DFT results for S/Ag(410) are also given in Fig. 7. Trends are very similar to S/Cu(410), including L-C being the overall favored site (though L-B is very close), and interactions at $\sqrt{2}a_s$ being repulsive for all configurations based on the comparison of $\mu_S$ for L and M groups.

V. DISCUSSION

To facilitate comparisons, all values of $\mu_X$ for vicinal surfaces from this work are given in Tables II and III. From these tables, and from the presentations in Secs. III and IV, several broad generalizations can be drawn. These generalizations apply to both Cu and Ag unless stated otherwise. We address the (211) surfaces first.

(211) surfaces. For the (211) surfaces, step reconstruction is important in all four systems (O/Cu, O/Ag, S/Cu, S/Ag). In

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Description</th>
<th>$\theta_X$</th>
<th>$\mu_O$ (O/Cu(211))</th>
<th>$\mu_O$ (O/Ag(211))</th>
<th>$\mu_S$ (S/Cu(211))</th>
<th>$\mu_S$ (S/Ag(211))</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-A</td>
<td>4fh</td>
<td></td>
<td>-1.722(2)</td>
<td>-0.666(2)</td>
<td>-2.242(2)</td>
<td>-1.408(2)</td>
</tr>
<tr>
<td>U-B</td>
<td>3fh hcp</td>
<td>0.204</td>
<td>-1.629(3)</td>
<td>-0.471(3)</td>
<td>-1.897(3)</td>
<td>-1.125(3)</td>
</tr>
<tr>
<td>U-C</td>
<td>3fh fcc</td>
<td></td>
<td>-1.824(3)</td>
<td>-0.561(4)</td>
<td>-2.038(4)</td>
<td>-1.210(4)</td>
</tr>
<tr>
<td>U-A2</td>
<td>Mixed: 3fh fcc + 4fh</td>
<td>0.408</td>
<td>-1.861(2)</td>
<td>-0.759(3)</td>
<td>-2.079(2)</td>
<td>-1.330(2)</td>
</tr>
<tr>
<td>R-A</td>
<td>4fh</td>
<td></td>
<td>-1.642(8)</td>
<td>-0.614(6)</td>
<td>-2.188(8)</td>
<td>-1.366(6)</td>
</tr>
<tr>
<td>R-B</td>
<td>3fh fcc</td>
<td></td>
<td>-1.606(9)</td>
<td>-0.487(16)</td>
<td>-1.819(9)</td>
<td>-1.090(7)</td>
</tr>
<tr>
<td>R-C</td>
<td>4fh</td>
<td>0.102</td>
<td>-1.992(7)</td>
<td>-0.829(27)</td>
<td>-2.429(8)</td>
<td>-1.538(5)</td>
</tr>
<tr>
<td>R-D</td>
<td>3fh fcc</td>
<td></td>
<td>-1.608(6)</td>
<td>-0.487(36)</td>
<td>-1.823(8)</td>
<td>-1.098(6)</td>
</tr>
<tr>
<td>R-E</td>
<td>3fh fcc</td>
<td></td>
<td>-1.643(6)</td>
<td>-0.494(24)</td>
<td>-1.922(6)</td>
<td>-1.137(4)</td>
</tr>
<tr>
<td>R-F</td>
<td>3fh hcp</td>
<td></td>
<td>-1.865(10)</td>
<td>-0.576(3)</td>
<td>-2.056(5)</td>
<td>-1.224(3)</td>
</tr>
<tr>
<td>R-A2</td>
<td>3fh fcc + 4fh</td>
<td>0.204</td>
<td>-2.024(2)</td>
<td>-0.857(2)</td>
<td>-2.198(3)</td>
<td>-1.436(2)</td>
</tr>
</tbody>
</table>
In location 6. This is supported by a systematic comparison of interactions between the adsorbate and adjacent metal atoms of the R-A2 structure. We postulate that there are repulsive gen. In the latter case, R-C can be regarded as a component to be R-C itself, as it is for sulfur, or R-A2, as it is for oxy-
tion is clear whether the most stable configuration is predicted in Fig. 3. The importance of R-C in stabilizing the reconstruc-
be the creation of the very stable 4fh site labeled R-C. This
from DFT. In all four systems, the driving force appears to one case, it has been observed experimentally and is supported by our DFT, while in the other three cases it is predicted solely from DFT. In all four systems, the driving force appears to be the creation of the very stable 4fh site labeled R-C. This 4fh site is different from the 4fh site which is available on the unreconstructed surface, U-A, because in R-C the adsorbate has no neighboring metal atoms at the location of metal atom 6 in Fig. 3. The importance of R-C in stabilizing the reconstruction is clear whether the most stable configuration is predicted to be R-C itself, as it is for sulfur, or R-A2, as it is for oxygen. In the latter case, R-C can be regarded as a component of the R-A2 structure. We postulate that there are repulsive interactions between the adsorbate and adjacent metal atoms in location 6. This is supported by a systematic comparison of $\mu_X$ for R-C and R-A (or U-A, which is very similar to R-A). These are all 4fh sites, but R-C is preferred over R-A in all four systems. The difference between R-C and R-A is smaller for Ag than for Cu, for a given adsorbate. This likely reflects the larger lattice constant of Ag compared with Cu, leading to a larger separation between the adsorbate and metal atom 6. Similar repulsion may also explain the relatively low stability of L-A among the low-coverage configurations in all four of the (410) systems.

Similar repulsions are also found for O on other surfaces vicinal to (100), as shown in the supplementary material for Cu(511) and Ag(511), and for O on vicinal Pd(100) surfaces. The reason for this repulsion is not entirely clear at this stage. It can be argued that this is an indirect interaction, in which the presence of Cu atom 6 increases the metal coordination of Cu atoms 3 and 4 [Figs. 3(a) and 3(b)], which in turn weakens bonding between Cu atoms 3, 4, and oxygen. While this is plausible, the fact that the apparent repulsion is sensitive to metal-oxygen distance (based on the comparison between Cu and Ag above) also indicates that there may be direct interactions between O and metal at this distance (around 0.3 nm).

For the (211) surfaces, it is also important to consider the possibility of the double-row zig-zag chain structures, U-A2 and R-A2. These have not been considered in prior calculations nor experimental interpretations. For oxygen, R-A2 is energetically competitive with R-C, though DFT cannot presently predict which is more stable because the energy difference between them is small, and their relative stability depends on the functional used. There are some indications that R-A2 was observed under one particular set of experimental conditions. For sulfur, the picture is different: R-A2 is much less stable than R-C, i.e., double-row structures are not favored.

The difference between sulfur and oxygen in terms of the relative stability of R-A2 is intriguing. Elsewhere, we have reported that (near-)linear S–M–S units are structural motifs of complexes that form between S and coinage metals $M$ on the Cu(111), Ag(111), and Au(100) surfaces. In the case of CuS$_2$ complexes, we showed that the linear geometry was favored because it maximized the overlap between S p-orbitals and Cu-d$_z^2$ orbitals.

The linearity of $X$–M–$X$ units may provide an explanation for the different relative stabilities of R-A2 for O and S. In the double-row structures, there is an interaction $\Delta$ between adsorbates, based on the fact that $\mu_O$ of the double-row is always different than the average of the constituent single-row structures. In Fig. 8(a), we show $\Delta$ as a function of the $X$–M–$X$ angle in the double row, $\varphi$, for all four (211) systems. Here $\Delta$ is defined as

$$\Delta(R-A2) = \mu_X(R-A2) - ([\mu_X(R-C) + \mu_X(R-F)]/2).$$

There is a clear correlation between $\Delta$ and $\varphi$, with $\Delta$ becoming more negative (R-A2 more favorable) as $\varphi$ approaches 180°. While this correlation does not prove causality, it certainly admits the possibility that the degree of linearity accessible to the $X$–M–$X$ unit at the step affects its stability. Linearity is geometrically less accessible with the smaller metal, Cu, or the larger adsorbate, S. The latter provides a steric rationale for the instability of R-A2 with S.
For oxygen, the (410) surfaces of both Cu and Ag are dominated by O–M\(\text{−}\)rows which form in oxygen-induced reconstructions of Cu(100), Cu(110), and Ag(110).\(^{53}\) We find that there is an attractive interaction between O atoms at the \(\sqrt{2}a_s\) separation but only when they lie along the top step edge. Oxygen in the M-D configuration is more stable than oxygen adsorbed on terraces—both on the (410) and the flat (100)—and hence M-D sites are expected to be populated with O atoms even at lowest \(\theta_O\). At higher coverage, terrace sites on the vicinal surface become competitive energetically, which results in the H-A configuration. These results are consistent with, and provide the first theoretical underpinning for, the experimental observations for O/Cu(410). Furthermore, they provide predictions for O/Ag(410). For sulfur, on the other hand, the M-D configuration is unstable relative to a lower-coverage configuration involving adsorption on the terrace 4fh sites, leading to a prediction that at low coverages, S atoms will actually avoid the (410) step edges.

The reason for the difference between S and O in terms of their preference for M-D is almost certainly linked to the interaction at \(\sqrt{2}a_s\) along the step. This interaction is attractive for O and repulsive for S, based on the comparison of \(\mu_O\) for M-D and L-D. Following the discussion of the (211), we speculate that the interaction energy may be related to the degree of linearity of the \(X–M–X\) unit at the step edge. Therefore, we define the interaction energy for M-D as

\[
\Delta(M-D) = \mu_X(M-D) - \mu_X(L-D).
\]

Fig. 8(b) again shows a clear correlation between \(\Delta\) and \(\phi\), with \(\Delta\) becoming more negative (M-D more favorable) as \(\phi\) approaches 180\(^\circ\). The same geometric trends are evident as well, i.e., less linearity and more positive \(\Delta\) for the smaller metal (Cu) or the larger adsorbate (S). We caution again that this correlation does not prove causality; (combinations of) factors such as metal coordination, charge transfer, and adsorption site symmetry may also contribute or at least provide an alternative framework for interpretation. However, \(\Delta\) vs. \(\phi\) straightforwardly accounts for the difference between O and S site preferences on both the (211) and (410) surfaces. We suggest that the linearity of \(X–M–X\) units should be considered a possible physical factor in stabilizing metal-adsorbate configurations whenever contiguous \(X–M–X\) chains are observed.

**VI. CONCLUSIONS**

In this paper, we have presented the results of extensive DFT calculations of adsorption site energetics for eight systems consisting of two chalcogens (O, S) adsorbed on two vicinal surfaces [(211) and (410)] of two coinage metals (Cu, Ag), with the goal of identifying the most stable adsorption configuration(s). For each system, we have analyzed multiple possible configurations. In general, the nature of the metal (Cu vs. Ag) makes little difference in relative stabilities of different configurations, while the nature of the chalcogen (O vs. S) leads to much stronger differences.

Our theoretical work connects with prior experimental results in different ways. In one case, it resolves an experimental ambiguity [O/Cu(410) at low \(\theta_O\)], and in another it provides the theoretical confirmation of a prior experimental conclusion [O/Cu(410) at high \(\theta_O\)]. It also calls into question an earlier assignment [O/Cu(211)]. In other cases, no data are available for comparison, so this work can be regarded as predictive in nature. For a few configurations, earlier high-level theoretical analyses have been carried out.\(^{11–13}\) Where comparison is possible, our results agree completely with those earlier calculations.

Calculations for the flat (111) and (100) surfaces show that chalcogen adsorption is always stronger on Cu than on Ag, and this is evident on the vicinal surfaces as well. These calculations also show that adsorption is stronger at 4fh sites of the (100) than at 3fh sites of the (111), other parameters being fixed. This site-preference plays a role on the vicinal surfaces, but the situation is also more complex.

Regarding the (211) surfaces, the major conclusions are as follows:

- The step-doubling reconstruction occurs in all four systems (O/Cu, O/Ag, S/Cu, S/Ag) and is driven by the
creation of the top 4fh site on the vertical wall of the (100) step (R-C). This site is more stable than the 4fh site available on the unreconstructed surface because of effective repulsion between the adsorbate and a metal atom above the plane of the 4fh site in the latter case.

- Double-row zig-zag chain structures must be considered. In these configurations, half of the adsorbate atoms occupy the very stable R-C site. For oxygen on the reconstructed (211) surfaces, such a configuration is energetically competitive with R-C alone and may be the experimentally observed structure. However, for sulfur, the zig-zag chain structure is much less stable than the 4fh R-C site, and zig-zag structures are not predicted.

- For O/Cu(211), the DFT result is in conflict with the experimental site assignment. This may mean that the original assignment should be reconsidered. Notably, the zig-zag chain structure was not envisioned in the original work.

Regarding the (410) surfaces, the major conclusions are as follows:

- For oxygen, a configuration consisting of O–M–O rows with oxygen atoms in the incomplete 4fh site on the top edge of the step (M-D), rather than the complete 4fh sites available on the terraces, is clearly most favorable. This resolves an experimental ambiguity in the site assignment.

- For sulfur on (410) surfaces, QSE can sometimes be mitigated when comparing properties calculated using the same supercell, where one can expect

SUPPLEMENTARY MATERIAL

See supplementary material for the following topics: illustrations of supercell names used in DFT as described in Sec. II; tabulated adsorption energies of O and S on the (111) and (100) surfaces of Cu and Ag, corresponding to Figs. 1 and 5; and μO and μS values for Cu(511) and Ag(511).

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APPENDIX: QUANTUM SIZE EFFECTS IN O/Cu(211)

Large variations of surface properties due to slab thickness due to the confinement of electrons in a finite region (quantum size effects) make determining the adsorption energies in the limit of practically semi-infinite systems using slab calculations computationally demanding. To illustrate this point, Fig. 9(a) shows μO as a function of the number of layers L of the R-C configuration for O/Cu(211) and of the (2 × 2) ordered O(4fh) on Cu(100). The x-axis is scaled as hL/a_b, where h is the interlayer spacing. Clear oscillatory behavior with a period of 0.6a_b can be observed for O/Cu(211). The period is consistent with the half Fermi wavelength of a Cu crystal in the free electron model. The oscillation is not as pronounced for O/Cu(100), which is due to the closeness between the interlayer spacing (0.5a_b) and the half Fermi wavelength.

QSE can sometimes be mitigated when comparing properties calculated using the same supercell, where one can expect...
QSE to be similar. However, this is not generally possible, and one would like to estimate a converged bulk limit. Here we use a simple averaging scheme by taking the arithmetic mean of the quantity of concern ($\mu_0$ in this case) evaluated over a range of slab thicknesses, starting from around $L_{\text{max}}/2$, where $L_{\text{max}}$ is the number of layers of the thickest slab calculated. Results using $L = 13–24$ for O/Cu(211) and $L = 7–12$ for O/Cu(100) are shown as horizontal bars in Fig. 9(a). The width of the bar represents our estimate of the numerical accuracy, which is calculated as the standard deviation of $\mu_0$ in this range of $L$ divided by $(N−1)$, where $N$ is the number of slabs averaged. Note that this is a more optimistic estimate than the estimate of statistical errors, which is the standard deviation divided by $\sqrt{N−1}$. This choice is partially empirical, and partially based on the observation that the data are oscillatory rather than randomly distributed, which allows for faster convergence.

Figure 9(b) shows similar plots of $\mu_0$ of the U-A configuration for O/Cu(211) and $(2 \times 2)$ ordered O in fcc sites on Cu(111). Again, the oscillatory feature is very noticeable on the vicinal surface, while disguised for the (111) surface with larger interlayer spacing.

Note that for both Figs. 9(a) and 9(b), very dense k-point grids are used to minimize the numerical errors due to incomplete Brillouin zone sampling. For example, for O(U-A) in Fig. 9(b), the k-point grid used is $(18 \times 7 \times 1)$, with $\mu_0 = −1.995 \pm 0.002$ eV. This agrees very well with the value of $−1.992 \pm 0.007$ eV listed in Table II and Fig. 2, using the standard procedure described in Sec. II, with $(12\times 5\times 1)$-k-point grid and 7 slabs ranging from 12–24.